Conformational properties of comb copolymer brushes: Persistence and Curvature

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Voor:

Simone
Heit
Mem
Titia

A mind is like a parachute. It doesn't work if it's not open.

- Frank Zappa

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Outline

The research reported in this thesis is concerned with the conformational properties of comb copolymer brushes in infinitely dilute solution. In particular the focus is turned towards stiffness and (spontaneous) curvature. The conformational properties of comb copolymer brushes in solvent may be influenced in various ways by designing a particular architecture, using variables such as topology and chemical composition, as well as by imposing certain conditions such as topological constraints, temperature, and solvent conditions.

This thesis consists of two main parts. The first of these provides some background and context to the research topic of this work in the form of three review chapters. The first chapter (Chapter 1) is concerned with the experimental aspects of cylindrical polymer brushes. It focuses mainly on the types of polymer brushes, based on architecture and (chemical) composition, that have been synthesized successfully over the last two decades rather than on the chemical details and the polymerization techniques. Using chemically different types of side chains in the same comb copolymer brush combined with the use of selective solvent it is possible to induce intra-molecular phase separation resulting, e.g. in so-called Janus micelles.

Next, the experimental characterization of the comb copolymer brush conformation in dilute solution is discussed. Using a combination of theoretical modelling and light scattering experiments physical quantities such as the radius of gyration, the Kuhn statistical segment size and the contour length per monomer can be evaluated. The discussion is complemented by an example using simulation data. Particularly noteworthy is the fact that the contour length per monomer is generally much smaller than the all-trans value, demonstrating that the polymer backbone is locally coiled rather than being fully stretched. Another very useful technique is the

visualization of molecular brush conformations by AFM. The observation of spiralling conformations for molecular brushes strongly adsorbed onto a flat substrate has spawned a number of theoretical studies discussing spontaneous curvature. This issue is being addressed in this thesis by computer simulation which will be discussed in Chapter 5. The review is concluded by discussing a number of applications of cylindrical polymer brushes such as molecular valves.

Chapter 2 discusses the theoretical aspects of comb copolymer brushes. It starts with outlining a scaling analysis of a comb copolymer brush having a straight backbone. Here the blob model is introduced and a relation between brush radius, grafting density and side chain length is reproduced. Next the free energy of the comb copolymer brush as a function of bending is calculated in analogy with the original work of Fredrickson. This analysis leads to a prediction on the scaling behavior of the persistence length with respect to grafting density and side chain length. Calculation of the ratio between the persistence length and the brush diameter leads to the prediction that if the side chains are long enough the comb copolymer brush becomes a very stiff object.

Scaling arguments and the blob model are employed to analyze spontaneous curvature of the 2D bottle brush. It is shown that scaling arguments predict the 2D bottle brush to be stable with respect to bending, contrary to the mean field analysis by Potemkin and coworkers. Experiments as well as the computer simulation study presented in Chapter 5 confirm the presence of spontaneous curvature. However, spontaneous curvature did not turn up in previous simulation studies and this matter will be discussed in Chapter 7.

Chapter 3 discusses Monte Carlo simulations on cylindrical polymer brushes. It starts out by giving a general introduction of Monte Carlo simulations and how these can be applied to polymer systems. In particular the bond fluctuation model (BFM) is discussed which has been used in all simulation studies reported in this thesis. In addition the so-called 'infinite lattice' approach is outlined which we developed to get rid of the need for very large simulation boxes such that simulations of large systems can be performed on computers with low memory, thus making it particularly useful for simulations on Beowulf type computer clusters. The chapter proceeds with a discussion of the literature on Monte Carlo simulations of branched polymers.

The second part of this thesis reports our simulation studies on the conformational behavior of comb copolymer brushes. Chapter 4 reports our study on the conformational aspects and intramolecular phase separation of alternating copolymacromonomers using the BFM. The architecture which is being investigated consists of a comb copolymer brush with two different types of side chains alternatingly grafted along the backbone. By evaluating angular correlation histograms we examine the phase separation of the side chains with increasing chemical incompatibility. Provided the backbone is stiff, we observe a pearl necklace-like transition in poor solvent. When the backbone is flexible it is possible to obtain meandering and horseshoe like conformations by imposing different solvent conditions on both side chain types.

Chapter 5 reports our simulation study discussing spontaneous curvature of comb copolymers strongly adsorbed at a flat surface. The simulations in this study are athermal and concern densely grafted 2D comb copolymers. Two different cases are investigated, the difference being whether the side chains are allowed to flip from one side of the backbone to the other side. When the side chains are allowed to flip the polymers display a distinct curvature. This is illustrated using bond angle correlation plots as well as scattering analysis. A theoretical model, including both curvature and stiffness, is outlined that is able to fit the data. The main findings are in agreement with recent theoretical and experimental studies.

Chapter 6 discusses our simulation study on cylindrical core-shell structures formed by dendrite-like polymers in selective solvent. Using dendronized side chains rather than linear side chains a core-shell structure is formed in selective solvent. Three cases are being distinguished: the athermal case in which the conformational properties are governed by excluded volume only, the case in which the shell experiences good solvent whereas the core experiences moderate solvent and the case in which the core experiences poor solvent. It is demonstrated, using bond angle correlation plots as well as scattering data, that the poor solvent case exhibits significantly different behavior from both other cases. The poor solvent case displays curvature whereas the other two show simple persistent wormlike chain behavior. Our theoretical model, discussed in Chapter 5 was found to be able to fit the data quite well. If persistence and curvature could be increased it may be possible to obtain ring closure depending on solvent conditions or temperature.

Chapter 7 discusses our simulation results on 2D comb copolymer brushes with a lower grafting density than those in Chapter 5. In that previous work it was suggested that the fact that spontaneous curvature did not turn up in other simulation studies is connected to the lower grafting density that was used there. Using the same model and conditions the grafting density has been decreased by a factor of three in Chapter 7. It is shown that spontaneous curvature is indeed lost and that the conformational properties of the comb copolymer are perfectly described as being persistent comb copolymer chain behavior. Our findings support the idea that a cross-over regime exists between lower grafting densities for which scaling analysis is valid and higher grafting densities for which scaling arguments are not acceptable anymore and mean field calculations have to be employed.